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**IMPACT OF REDUCED GRAPHENE OXIDE ON MoS₂
GROWN BY SULFURIZATION OF SPUTTERED MoO₃
AND Mo PRECURSOR FILMS (POSTPRINT)**

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14. ABSTRACT (Maximum 200 words) Monolayer molybdenum disulfide (MoS2), a two dimensional semiconducting dichalcogenide material with a bandgap of 1.8–1.9 eV, has demonstrated promise for future use in field effect transistors and optoelectronics. Various approaches have been used for MoS2 processing, the most common being chemical vapor deposition. During chemical vapor deposition, precursors such as Mo, MoO3, and MoCl5 have been used to form a vapor reaction with sulfur, resulting in thin films of MoS2. Currently, MoO3 ribbons and powder, and MoCl5 powder have been used. However, the use of ribbons and powder makes it difficult to grow large area-continuous films. Sputtering of Mo is an approach that has demonstrated continuous MoS2 film growth. In this paper, the authors compare the structural properties of MoS2 grown by sulfurization of pulse vapor deposited MoO3 and Mo precursor films. In addition, they have studied the effects that reduced graphene oxide (rGO) has on MoS2 structure. Reports show that rGO increases MoS2 grain growth during powder vaporization.					
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Impact of reduced graphene oxide on MoS₂ grown by sulfurization of sputtered MoO₃ and Mo precursor films

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Monolayer molybdenum disulfide (MoS₂), a two dimensional semiconducting dichalcogenide material with a bandgap of 1.8–1.9 eV, has demonstrated promise for future use in field effect transistors and optoelectronics. Various approaches have been used for MoS₂ processing, the most common being chemical vapor deposition. During chemical vapor deposition, precursors such as Mo, MoO₃, and MoCl₅ have been used to form a vapor reaction with sulfur, resulting in thin films of MoS₂. Currently, MoO₃ ribbons and powder, and MoCl₅ powder have been used. However, the use of ribbons and powder makes it difficult to grow large area-continuous films. Sputtering of Mo is an approach that has demonstrated continuous MoS₂ film growth. In this paper, the authors compare the structural properties of MoS₂ grown by sulfurization of pulse vapor deposited MoO₃ and Mo precursor films. In addition, they have studied the effects that reduced graphene oxide (rGO) has on MoS₂ structure. Reports show that rGO increases MoS₂ grain growth during powder vaporization. Herein, the authors report a grain size increase for MoS₂ when rGO was used during sulfurization of both sputtered Mo and MoO₃ precursors. In addition, our transmission electron microscopy results show a more uniform and continuous film growth for the MoS₂ films produced from Mo when compared to the films produced from MoO₃. Atomic force microscopy images further confirm this uniform and continuous film growth when Mo precursor was used. Finally, x-ray photoelectron spectroscopy results show that the MoS₂ films produced using both precursors were stoichiometric and had about 7–8 layers in thickness, and that there was a slight improvement in stoichiometry when rGO was used. © 2016 American Vacuum Society.

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I. INTRODUCTION

Molybdenum disulfide (MoS₂) has attracted much attention due to its direct bandgap of 1.8–1.9 eV observed in monolayer thick MoS₂ films,^{1,2} making MoS₂ an attractive two dimensional (2D) semiconducting material for low power electronic and optoelectronic devices.^{3,4} Growth processes of 2D MoS₂ include mechanical exfoliation,^{5–7} chemical vapor deposition (CVD),^{1,2} intercalation assisted exfoliation,^{8–11} physical vapor deposition (PVD),^{12,13} and a wet chemistry approach involving thermal decomposition of a precursor containing Mo and S.¹⁴ Among these, mechanical exfoliation and CVD are the most common procedures

currently used to produce mono- to few layers of MoS₂. In contrast to mechanical exfoliation, the growth of MoS₂ by CVD can enable large area films for device fabrication. Molybdenum disulfide films grown using CVD has demonstrated promising results for semiconductor grade material properties, with observed FET mobilities around 500 cm²/V s.¹⁵ During CVD growth, sulfurization of molybdenum containing precursors such as Mo, MoO₃, and MoCl₅ is usually performed. In the case of MoO₃ (Ref. 2) and MoCl₅,¹⁶ powders or ribbons are the precursors, whereas Mo has been prepared by e-beam evaporation¹ or sputtering.¹⁷ While the use of these powder and ribbon precursors have demonstrated large crystal growth,¹⁵ it is difficult to continuously grow these large domains over an entire wafer. In addition, the presence of grain boundaries prevents optimum device

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TABLE I. List of thickness used for Mo and MoO₃ precursor films. *r* indicated rGO was used during experiments.

Sample (<i>r</i> -rGO)	Precursor	Precursor thickness (nm)
S1, S1 <i>r</i>	Mo	3
S2, S2 <i>r</i>	MoO ₃	3

performance. Lee *et al.*¹⁸ reported that seed promoters such as reduced graphene oxide (rGO), perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS), and 3,4,9,10-perylene-tetracarboxylic acid dianhydride improved layer growth of CVD grown MoS₂.¹ Ling *et al.*¹⁹ furthers the investigation and demonstrates an increase in domain size when seed promoters are used during MoS₂ synthesis. In this work, we investigate the impact of rGO on MoS₂ grown by sulfurization of MoO₃ and Mo precursor films at room temperature. While CVD growth of MoS₂ films using RF sputtered MoO₃ precursors has been reported,²⁰ our work consists of using DC magnetron sputtered Mo and MoO₃ films. Sputtering of precursor films, followed by sulfurizing, has demonstrated continuous film growth of MoS₂.¹⁷ Sputtering and other PVD approaches for precursor film preparations have advantages in uniformly covering large substrate areas, which can lead to large area 2D film synthesis, an advantage over using powder and ribbon precursors. X-ray photoelectron spectroscopy (XPS) was performed to confirm the chemical composition, and transmission electron microscopy (TEM) was used to examine the MoS₂ structure. Finally, surface morphology of the MoS₂ film was investigated with atomic force microscopy (AFM).

II. EXPERIMENT

Thin films of metallic Mo and MoO₃ were sputtered on c-face sapphire substrates (diameter of 25.4 mm) using a DC magnetron sputtering system (500 V at 100 mA) at room temperature, with an argon pressure of 0.92 Pa. The thickness of the precursor (3 nm for both Mo and MoO₃) was controlled by manipulating the sputtering so that there were equal amounts of Mo sputtered in the MoO₃ and Mo films. Table I lists the precursors and names of the sample. The substrates were ultrasonically cleaned in acetone for 5 min prior to deposition of Mo and MoO₃. Following sputtering of Mo and MoO₃ onto the substrates, the precursors were separately placed at the center of the quartz tube (Fig. 1). Sulfur powder (2 g) was placed in a ceramic boat, upstream from the Mo and MoO₃ films. Reduced graphene oxide (Sigma Aldrich) was dispersed in isopropyl alcohol and drop cast on separate sapphire substrates. The rGO samples were air dried before they were placed in the furnace next to the sputtered precursor films of Mo and MoO₃ (a distance of 5 mm between the precursor and rGO samples). After pumping the furnace down to a vacuum pressure of 667 Pa, the samples were heated to 300 °C at 20 °C/min and held there for 15 min. This enabled the removal of any residual water molecules. Next, the furnace was heated to 850 °C at a rate of 20 °C/min. As the temperature of the furnace approached 850 °C (around 830 °C), the boat with sulfur was heated to 125 °C using a heating tape. The samples and the sulfur were held at their temperatures for 1 h, followed by cooling to room temperature. All experiments were performed in an Ar/H₂ environment, with a flow rate of 75 sccm.

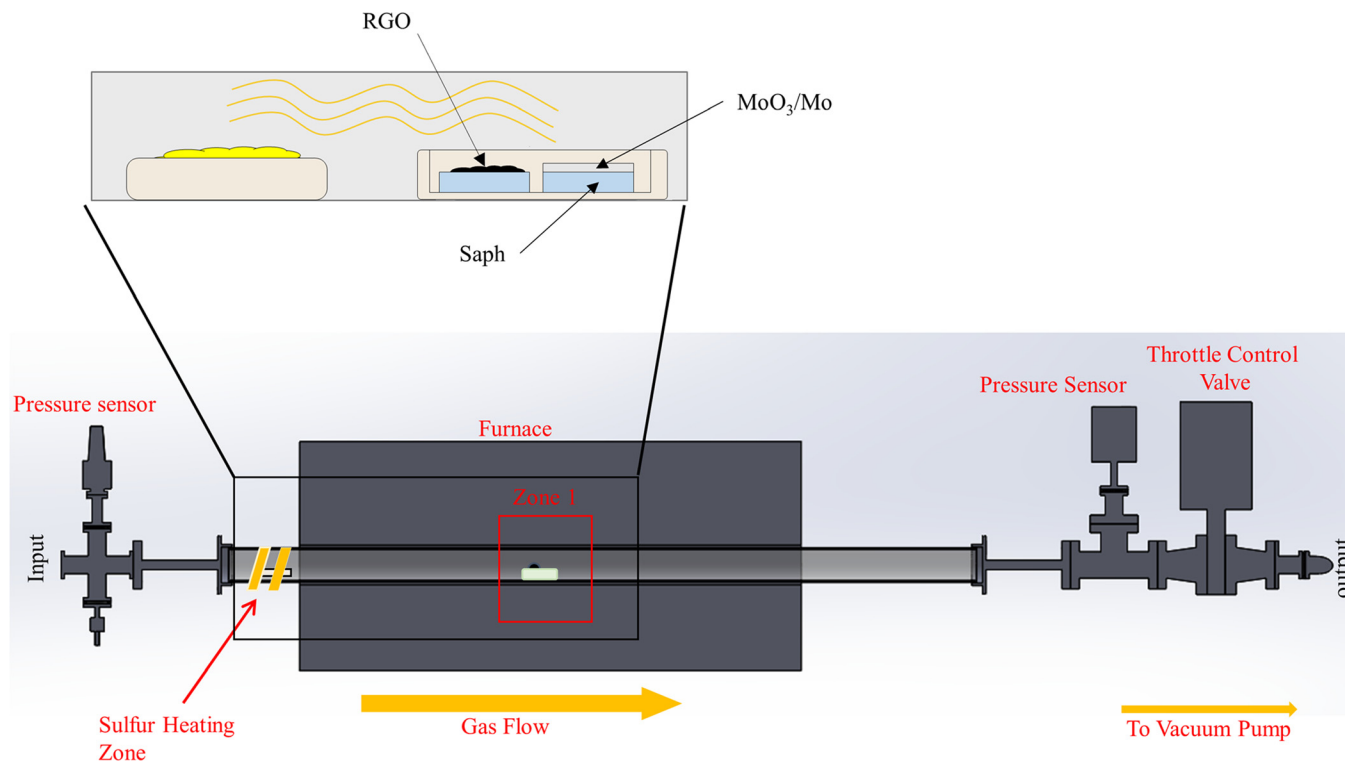


FIG. 1. (Color online) Chemical vapor deposition setup for MoS₂ growth on Al₂O₃ substrates.

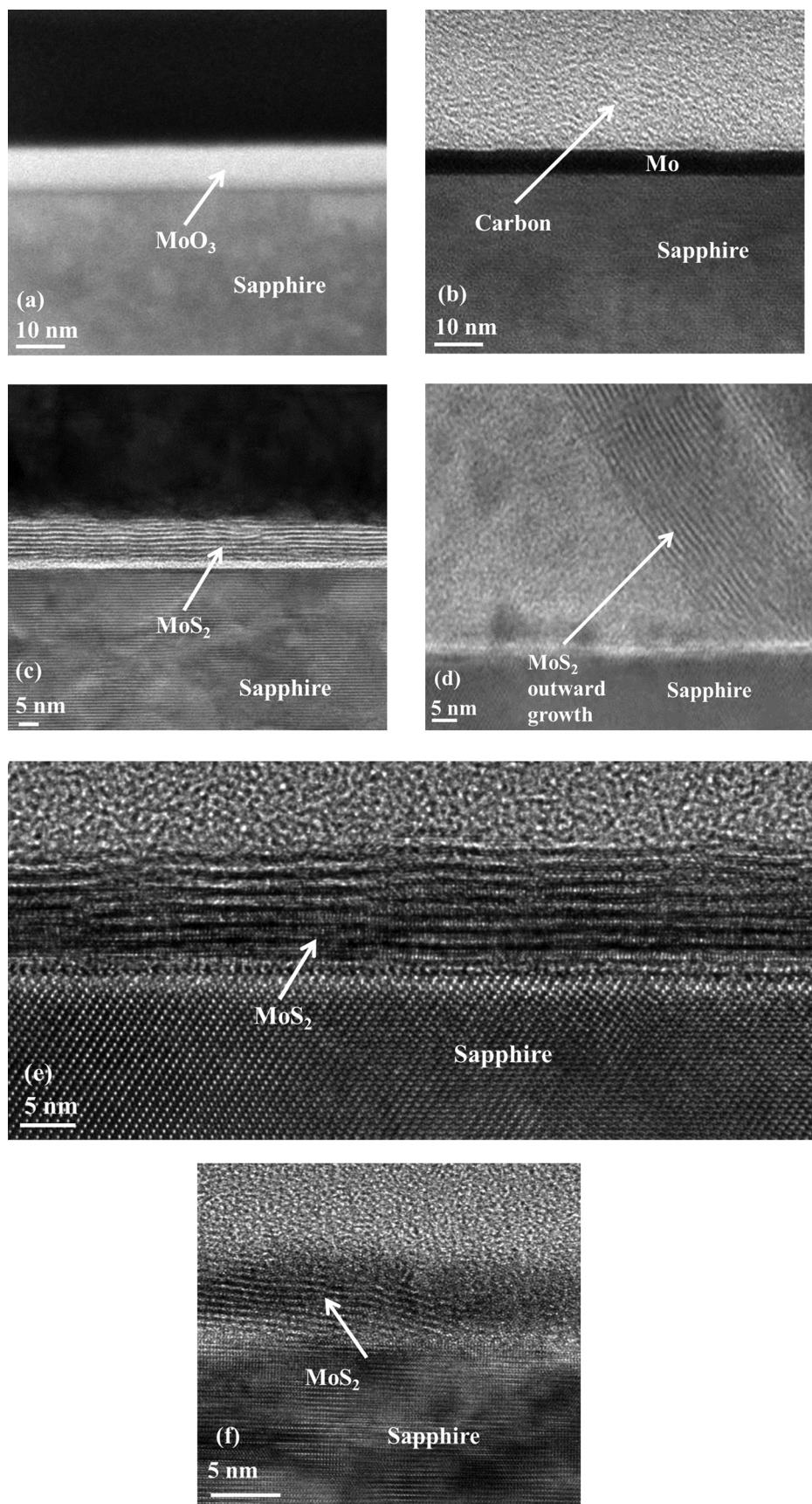


FIG. 2. TEM image of (a) MoO₃ precursor film used for MoS₂ growth, (b) Mo precursor film for MoS₂ growth, (c) sample S1 (MoS₂ on sapphire using Mo precursor) showing a layer thickness of 7 nm, (d) sample S2 (MoS₂ on sapphire using a MoO₃ precursor) showing an outward growth of MoS₂, with a thickness of 15 nm, (e) sample S1r (Mo precursor) using rGO with a measured thickness of 7–8 nm, and (f) sample S2r (MoO₃) using rGO with a thickness of 7 nm.

A. Characterization

AFM images were taken in an Asylum MFP-3D system in the tapping mode. Images were 512×512 pixels, and the scan speed was 1 Hz (1 line per second). The nominal radius of

curvature for the probe tips was 9 nm. The structure of the MoS₂ film was observed in a high-resolution TEM. Images were taken using a FEI Titan 80-300 S/TEM, which was operated at 300 kV. A FEI Nova focused ion beam (FIB) microscope equipped with

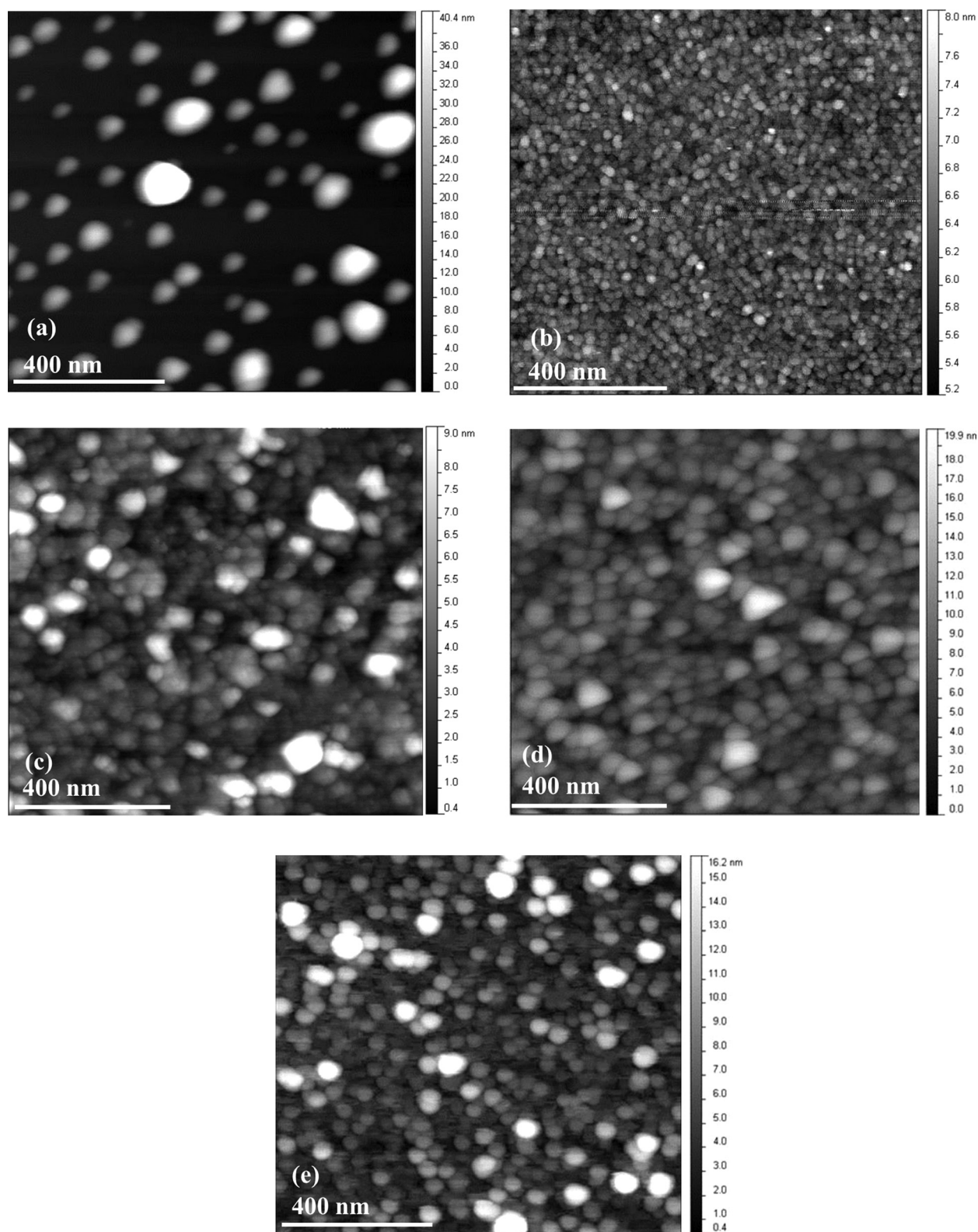


FIG. 3. AFM surface topography ($1 \times 1 \mu\text{m}$) for (a) MoO₃ precursor that was heated to 850 °C forming MoO₂ islands, (b) sample S1 (Mo precursor) showing a dense film of MoS₂ with a grain size of 4.4 nm, (c) MoS₂ sample S2 (MoO₃ precursor) with a grain size of 7.9 nm, (d) MoS₂ sample S1r (Mo precursor with rGO) with a grain size of 17.7 nm, and (e) MoS₂ sample S2r (MoO₃ precursor with rGO) with grain size of 12.2 nm.

an Omniprobe manipulator was employed to prepare the cross-sectional specimens. X-ray photoelectron spectroscopic analysis was carried out using a Phi Model 5700 spectrometer with a monochromatic Al K α x-ray source (1486.6 eV) operated at 75 W (15 kV, 5 mA) and at approximately 1.5×10^{-12} Torr.

III. RESULTS AND DISCUSSION

A. MoS₂ film structure and grain size

TEM imaging of the MoS₂ film cross-sections for samples S1 (MoS₂ grown from Mo precursor) and S1r (MoS₂ film

grown using Mo precursor with rGO seed) is shown in Fig. 2. The precursor films, MoO₃ and Mo, are both shown in Figs. 2(a) and 2(b). Samples S1 and S1r [Figs. 2(c) and 2(e)] show uniform and continuous layer growth of MoS₂. Both samples have a thickness of 7–8 nm, indicating that rGO used during the CVD growth of sample S1r had no effect on the film thickness. AFM showed samples S1 and S1r had an RMS of 360 and 2.43 nm (respectively), and the grain size increased from 4.5 to 17.7 nm, respectively [see Figs. 3(a) and 3(b)]. This increase in the grain size indicated that the

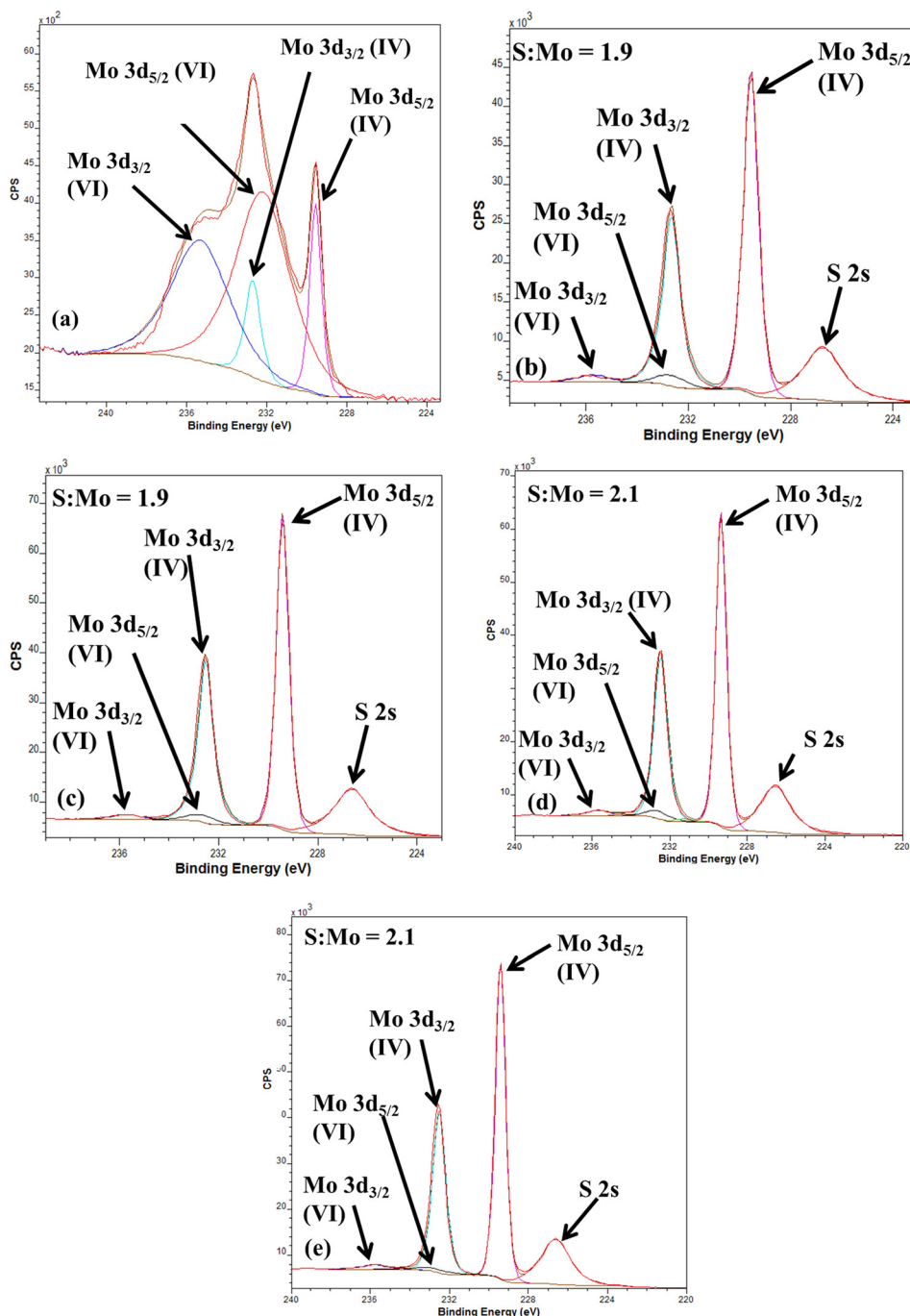


FIG. 4. (Color online) XPS spectra of annealed MoO₃, MoS₂ films S1 (MoS₂ using Mo precursor), S2 (MoS₂ using MoO₃ precursor), S1r (MoS₂ using Mo precursor and rGO), and S2r (MoS₂ using MoO₃ precursor and rGO). The annealed MoO₃ (a) shows Mo(IV) peaks which are indicative of MoO₂, and Mo(VI) peaks that occur when MoO₃ is present. Both (b) and (c) shows spectra for samples S1 and S2 (respectively) having a stoichiometric structure. In (d) and (e), the stoichiometry has been increased for samples S1r and S2r (respectively).

rGO played a role in grain growth of the MoS₂. In contrast to the uniform and continuous film growth of samples S1 and S1r, samples S2 (MoO₃ precursor) and S2r (MoO₃ precursor with rGO seed) demonstrated a nonuniform, outward growth of MoS₂ [Figs. 2(d) and 2(f)]. It is reported that at 600 °C, MoO₃ reduces to MoO₂ under an H₂ environment.²¹ In this research, it was indicated that MoO₂ had formed after annealing MoO₃ at 850 °C. X-ray photoelectron spectra [Fig. 4(a)] showed peaks at 229.57 and 232.7 for Mo(IV) (typical of MoS₂ and MoO₂) and 232.19 and 235.32 for Mo(VI) (typical of MoO₃). AFM was performed on the same annealed sample [Fig. 3(c)], and we noticed small islands across the substrate. We believe that these islands were formed when the sputtered MoO₃ film reduced to MoO₂ during annealing at 850 °C. Consequently, sulfurization of MoO₂ islands causes MoS₂ growth in a Volmer–Weber growth mechanism, which is a result of the film not wetting the substrate.²² Moser and Levy reported similar growth patterns using sputtering technique to deposit thick MoS₂ films.²³

Figures 3(d) and 3(e) show the grain structures of MoS₂ grown using the sputtered MoO₃ films (S2 and S2r). The RMS values for these samples were 2.00 nm (S2) and 3.66 nm (S2r), and the grain size increased from 7.9 nm (S2) to 12.2 nm (S2r) when rGO was used during the growth. This correlates well with the data from samples S1 and S1r that suggest that rGO promotes grain growth when using sputtered precursor films. There was also a decrease in the film thickness, from 15 nm (S2) to 7 nm (S2r) when rGO was used during the sulfurization process [Figs. 2(d) and 2(f)]. Ling *et al.*¹⁹ reports that organic seed promoters (such as PTAS) enable heterogeneous nucleation sites and that the size of the MoS₂ domains is dependent upon the distance of the seed promoter from the precursor. We believe this is what occurred when rGO was used in our experiments involving sputtered Mo and MoO₃ films. However, further investigation needs to be conducted to better understand the kinetics, and mechanism of increasing grain size, when using rGO during the sulfurization sputtered films.

B. MoS₂ chemical composition

XPS analysis was performed in order to assess the composition and chemistry of the films. The survey spectra (not shown) from sulfurized thin films of samples S1/S1r and S2/S2r showed peaks from Mo and S, as expected. As mentioned previously, Fig. 4(a) shows the spectra for annealed MoO₃, which was discussed in Sec. III A. The influence of the rGO on MoS₂ stoichiometry was analyzed by comparing the S:Mo ratios obtained from the XPS spectra. The MoS₂ films grown from samples S1 and S1r had S:Mo ratios of 1.9 and 2.1, respectively [see Figs. 4(b) and 4(d)]. Samples S2 and S2r demonstrated the same respective S:Mo ratios of 1.9 and 2.1 [see Figs. 4(c) and 4(e)]. The apparent improvement in the film stoichiometry is most likely a result of the Mo:S averaging over large spot size analysis area in XPS, which is orders of magnitude larger when compared to the average grain sizes of synthesized MoS₂ films. The presence of the

rGO helped to increase the MoS₂ grain size areas and correspondingly decrease contributions of photoelectrons escaped from the grain boundary areas.

Curve fits to the Mo 3d doublets for all of the samples revealed two populations of Mo atoms. The Mo 3d_{5/2} peak at 229.8 eV and Mo 3d_{3/2} peak at 232.9 eV reveal the presence of Mo(IV), with a binding energy typical of MoS₂ or MoO₂.²⁴ The Mo 3d_{5/2} peak at 232.7 eV and Mo 3d_{3/2} peak at 235.8 eV indicates the presence of Mo(VI), with a binding energy typical of MoO₃.²⁵ This suggests that while nearly all of the Mo(IV) is present in the form of MoS₂, there is likely some MoO₂ present at the surface or at grain boundaries within the films. However, the intensity of both the Mo(IV) and Mo(VI) peaks are very low that the presence of MoO₂ and MoO₃ is negligible.

IV. SUMMARY AND CONCLUSIONS

The influence of rGO on the sulfurization of metallic Mo and MoO₃ thin film precursors for MoS₂ growth has been investigated. TEM established that rGO did not have an impact on the MoS₂ films thickness for sputtered Mo, but that it was responsible for the increase in the grain size. We also observed an increase in the grain size when rGO was used during sulfurization of sputtered MoO₃. Reports demonstrate that seed promoters diffuse onto growth substrates, acting as nucleation sites for MoS₂ growth.¹⁹ In addition, the size of the MoS₂ domains are dependent upon the distance between the seed promoter and the growth substrate. Further investigations are being conducted to explain the kinetics involved when rGO is used during sulfurization of sputtered Mo and MoO₃. Nevertheless, the nanocrystalline size of our MoS₂ films would not make them suitable candidates for electronic devices. However, these nanocrystalline films are potentially applicable for optoelectronics.

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¹Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, and J. Lou, *Small* **8**, 966 (2012).

²S. Najmaei *et al.*, *Nat. Mater.* **12**, 754 (2013).

³B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nat. Nanotechnol.* **6**, 147 (2011).

⁴Z. Yin *et al.*, *ACS Nano* **6**, 74 (2012).

⁵B. Radisavljevic, M. B. Whitwick, and A. Kis, *ACS Nano* **5**, 9934 (2011).

⁶K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).

⁷J. Brivio, D. T. L. Alexander, and A. Kis, *Nano Lett.* **11**, 5148 (2011).

⁸H. S. S. R. Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati, and C. N. R. Rao, *Angew. Chem. Int. Ed.* **49**, 4059 (2010).

⁹Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, and H. Zhang, *Angew. Chem. Int. Ed.* **50**, 11093 (2011).

¹⁰V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, *Science* **340**, 1226419 (2013).

¹¹G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, *Nano Lett.* **11**, 5111 (2011).

¹²C. Muratore and A. A. Voevodin, *Thin Solid Films* **517**, 5605 (2009).

¹³C. Muratore *et al.*, *Appl. Phys. Lett.* **104**, 261604 (2014).

¹⁴C. Altavilla, M. Sarno, and P. Ciambelli, *Chem. Mater.* **23**, 3879 (2011).

¹⁵H. Schmidt *et al.*, *Nano Lett.* **14**, 1909 (2014).

¹⁶Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, and L. Cao, *Sci. Rep.* **3**, 1866 (2013).

- ¹⁷N. Choudhary, J. Park, J. Y. Hwang, and W. Choi, [Appl. Mater. Interfaces](#) **6**, 21215 (2014).
- ¹⁸Y.-H. Lee *et al.*, [Adv. Mater.](#) **24**, 2320 (2012).
- ¹⁹X. Ling, Y. H. Lee, Y. Lin, W. Fang, L. Yu, M. S. Dresselhaus, and J. Kong, [Nano Lett.](#) **14**, 464 (2014).
- ²⁰S. Hussain *et al.*, [Nanoscale](#) **8**, 4340 (2016).
- ²¹E. Lalik, W. I. F. David, P. Barnes, and J. F. C. Turner, [J. Phys. Chem. B](#) **105**, 9153 (2001).
- ²²D. L. Smith, *Thin Film Deposition* (McGraw-Hill Education, New York, 1995).
- ²³J. Moser and F. Levy, [J. Mater. Res.](#) **7**, 734 (1992).
- ²⁴G. Seifert, J. Finster, and H. Mueller, [Chem. Phys. Lett.](#) **75**, 373 (1980).
- ²⁵P. A. Spevack and N. S. McIntyre, [J. Phys. Chem.](#) **96**, 9029 (1992).